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1. *Preparation of Phthalocyanine-like Pigments related to the Porphyrins.*

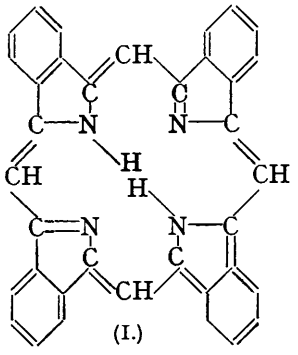
By CHARLES ENRIQUE DENT.

Methylenephthalimidine has been prepared by crystallising phthalimideneacetic acid from water at 80°. It is a stable yellow crystalline compound which readily polymerises when heated. Phthalonitrile, a metal compound, and either methylenephthalimidine or phthalimideneacetic acid readily react together to give new pigments, of which the copper derivative has been identified as *copper tetrabenzotriazaporphin*. The new pigments are green to blue and resemble in properties the phthalocyanines, to which they are closely related.

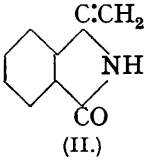
Benzylidenephthalimidine and ethylidenephthalimidine also have been prepared by new and improved methods.

IT has been shown (Dent, Linstead, and Lowe, J., 1934, 1933) that there exists a close similarity in structure between the phthalocyanines and the porphyrins; it seemed reasonable to suppose, therefore, that the technique used for preparing phthalocyanines could be applied to the synthesis of substances of true porphyrin structure.

The object of this work was to prepare derivatives of tetrabenzoporphin (I), *i.e.*, phthalocyanine in which the four "linking" nitrogen atoms are replaced by methin groups. It was considered that compounds of this type would be most readily prepared



(I.)



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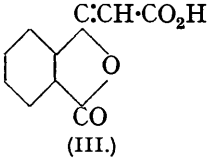

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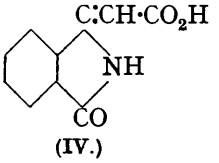


(IV.)

from intermediates which are known to give phthalocyanines but in which one nitrogen atom is replaced by a methin group. *o*-Cyanophenylacetylene has already been examined, without result, by Linstead and Noble (J., 1937, 934) and, acetylenic compounds being perhaps unsuitable on account of their instability, attention was concentrated upon *o*-cyanoacetophenone and *methylenephthalimidine* (II). The present paper describes the preparation and properties of methylenephthalimidine and some closely related compounds.

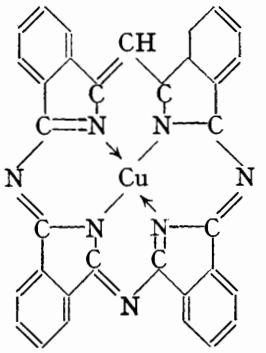
Phthalic anhydride was condensed with potassium acetate in the presence of acetic

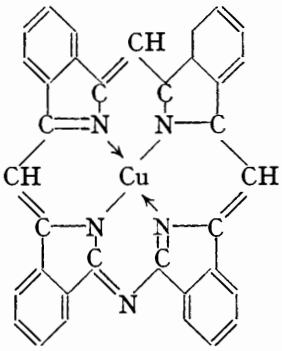
anhydride to give phthalideneacetic acid (III) (Gabriel and Neumann, *Ber.*, 1893, **26**, 951), which was converted, by solution in dilute aqueous ammonia and precipitation with hydrochloric acid (Gabriel, *Ber.*, 1877, **10**, 1556; Roser, *Ber.*, 1884, **17**, 2623), into phthalimideneacetic acid (IV). This acid lost carbon dioxide on crystallising from water at 70—90°, giving methylenephthalimidine. All these compounds polymerise readily at about 100°.

The action of methylmagnesium iodide upon phthalimide, of formaldehyde upon phthalimidine, and of ammonia upon methylenephthalide failed to give methylenephthalimidine.

Methylenephthalimidine, when heated with a metallic compound (cf. iminophthalimidine; Dent, Linstead, and Lowe, *loc. cit.*), alone or in presence of phosphoryl chloride, aluminium chloride, or chlorosulphonic acid in a suitable solvent, did not give a compound resembling a porphyrin or a phthalocyanine. When, however, a mixture of phthalonitrile, methylenephthalimidine or the more readily available phthalimideneacetic acid, and copper was heated, it readily gave a pigment greener than copper phthalocyanine, together with some resinous matter. This reaction was investigated further. The usual procedure was to mix equimolecular proportions of phthalonitrile and phthalimideneacetic acid with half the molecular proportion of the metal compound. In order to avoid undue polymerisation the mixture was either immersed in a bath at 250° or added direct to chloronaphthalene at 250°. The new coloured compound was formed in good yield in a few minutes. The product thus obtained by means of cupric or cuprous chloride was identified as *copper tetrabenzotriazaporphin* * (V). It is noteworthy that an unchlorinated compound is formed from cupric chloride. In the corresponding phthalocyanine reaction (Dent and Linstead, J., 1934, 1028) a monochlorinated phthalocyanine results.

(V.)





(IX.)

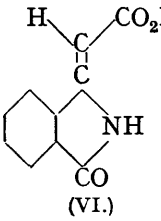
It seemed remarkable that methylenephthalimidine (or phthalimideneacetic acid) should react only in the presence of phthalonitrile and moreover that the combining proportions should be different from the proportions taken for reaction. The same product was obtained when the latter proportions were varied considerably. Although the analyses were conclusive, an independent check was considered advisable. Accordingly 4-chlorophthalonitrile was brought into reaction with an equimolecular proportion of phthalimideneacetic acid in the presence of cuprous chloride under the usual conditions. The purified *product* was greener than but otherwise similar in properties to the corresponding compound from phthalonitrile. It appeared to be homogeneous and contained exactly three chlorine atoms per molecule. This proves that there are three phthalonitrile units and one methylenephthalimidine unit in the pigment molecule.

N-Methylphthalimideneacetic acid (Gabriel, *Ber.*, 1885, **18**, 2451) did not react with phthalonitrile and cupric chloride, as would be expected owing to the absence of the imino-hydrogen atom.

The reaction of different metallic compounds with the mixture of phthalonitrile and phthalimideneacetic acid appears to be as general as the reaction with phthalonitrile alone. Other metallic derivatives have been obtained, all closely resembling the correspond-

* Nomenclature according to Helberger, *Annalen*, 1937, **529**, 205.

ing phthalocyanines in chemical and physical properties. They will be described in a later paper.



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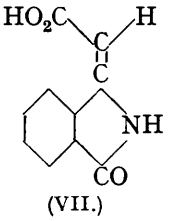

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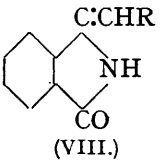


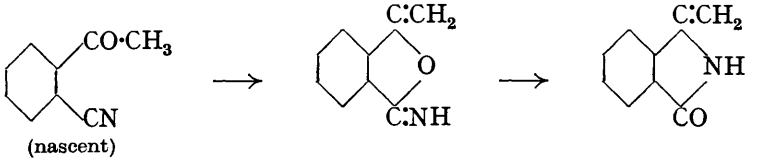
(VIII.)

There are two possible stereoisomeric forms of phthalimideneacetic acid (VI and VII). The presence of a hydrogen atom in the position *cis* to the imino-group is apparently necessary in order that the compound may enter into the porphyrin molecule, since the *trans*-atom is clearly the one which remains. It is believed that phthalimideneacetic acid has the structure shown in (VI) for the following reasons: complete decarboxylation always occurred; this would not be necessary in the case of (VII): protection of the carboxyl group by esterification or by conversion into its copper salt completely inhibited its reactivity in the presence of phthalonitrile.

Ethylidenephthalimidine (VIII, R = Me) has been prepared by an analogous method to the methylene compound starting from α-phthalidenepropionic acid and by treating ethylidenephthalide with ammonia. It appears to be identical with the compound prepared by Beis (*Compt. rend.*, 1904, **138**, 988; **139**, 62) by the action of ethylmagnesium bromide on phthalimide. It is a stable white crystalline compound not exhibiting the tendency towards polymerisation shown by the methylene compound. The reaction with phthalonitrile is being investigated.

Benzylidenephthalimidine (VIII, R = Ph) was prepared by passing ammonia into molten benzylidenephthalide. It is a yellow crystalline compound soluble in most organic solvents but most suitably crystallised from glacial acetic acid. Its chemical properties are under investigation.

Helberger (*Annalen*, 1937, **529**, 205) has described the preparation of porphyrin-like pigments by heating together *o*-chloroacetophenone and cuprous cyanide in quinoline. In this way he has prepared copper tetrabenzomonoazaporphin (IX), which he assumes is formed by the interaction of three molecules of nascent *o*-cyanoacetophenone with one molecule of phthalonitrile. The formation of the latter compound, seemingly by replacement of both the substituents of the *o*-chloroacetophenone, is remarkable and he suggests that the presence of phthalonitrile is necessary to start the reaction of the *o*-cyanoacetophenone. There is a fundamental similarity here with the behaviour of methylenephthalimidine. On the other hand, Helberger obtained products with three "linking" methin groups, whereas those described in this paper contain only one. It is difficult to agree, therefore, with Helberger that methylenephthalimidine is an intermediate in the formation of his products, though this could occur in the following stages:



(nascent)

The writer is indebted to Dr. R. P. Linstead for reminding him of the similarity between the last stage depicted above and the well-known molecular rearrangement of *o*-cyanobenzoic acid to phthalimide.

Experimental.

Preparation of Phthalideneacetic Acid (III) (modification of the method of Gabriel and Neumann, *loc. cit.*).—270 G. of phthalic anhydride were dissolved in 360 c.c. of acetic anhydride at 100°, 180 g. of fused potassium acetate added, and the temperature raised during 15 minutes to 150° and maintained, if necessary, for the completion of the reaction. The

mass thickened, then thinned, and finally set hard and showed a purple colour on the surface. At this stage it was withdrawn from the bath (to avoid polymerisation), cooled, added in small amounts to a large volume of water, washed with hot water and with alcohol, and dried at 60°. Yield, 140—160 g. of a pale brown solid insoluble in low-boiling organic liquids and completely soluble in dilute aqueous ammonia. Increasing the amount of potassium acetate to 270 g. gave a yield of 190 g. of good quality acid.

Preparation of Phthalimideneacetic Acid (IV) (after Gabriel and Roser, *locc. cit.*).—40 G. of phthalideneacetic acid were added to 40 c.c. of concentrated aqueous ammonia and 400 c.c. of water at 0—5°. After 30 minutes' stirring, the wine-red solution was filtered and made acid to Congo-paper by the gradual addition of dilute hydrochloric acid (1 : 1), the temperature being maintained at 0—5°. The precipitated phthalimideneacetic acid was collected after 30 minutes, washed with cold water, and dried at 40°. Yield, 38 g. of reddish crystalline acid containing two molecules of water of crystallisation. It could be purified by dissolving it in a slight excess of ammonia solution and precipitating it with a slight excess of hydrochloric acid (Found: C, 53·35; H, 4·4; N, 6·25. Calc. for $C_{10}H_7O_3N,2H_2O$: C, 53·3; H, 4·9; N, 6·2%). The author was unable to check Gabriel's observation that phthalimideneacetic acid could be purified by crystallisation from hot water, methylenephthalimidine being always obtained. The solution in water was acid to Congo-red, but became neutral on boiling. The dihydrate melted at 120° with instant effervescence; on further heating a resinous polymer was obtained.

Preparation of Methylenephthalimidine.—24 G. of phthalimideneacetic acid dihydrate, added to 600 c.c. of water at 80°, rapidly dissolved and effervesced vigorously. At the moment the gas evolution appeared to be nearly complete the solution was filtered through a preheated funnel into a flask immersed in ice, and cooled rapidly as possible by swirling. *Methylenephthalimidine* separated in golden-yellow crystals, which were collected after 30 minutes, washed with cold water, and dried at 40°. Yield, 11 g. The time of solution and decomposition at 80° was most critical and was usually about 30—60 seconds. It was difficult to obtain a product with the full carbon content, owing to the likelihood of contamination with undecarboxylated material. On the other hand, if the substance was maintained too long at 80°, a milkiness due to polymerisation soon developed; this always contaminated the product, since it passed through the filter paper in the first filtration (Found: C, 73·4, 73·3; H, 4·65, 4·7; N, 9·7; *M*, cryoscopic in phenol, 140±10. C_9H_7ON requires C, 74·5; H, 4·8; N, 9·7%; *M*, 145).

Methylenephthalimidine melts when immersed in a bath at 120—125°. If slowly heated, it sinters at about 230° and melts at 250—260° owing to polymerisation. When heated to a higher temperature, it rapidly polymerises to a resinous substance, hard and brittle when cold and usually red. It is readily soluble in cold acetone, methanol, and other organic solvents, but much less so in warm water. When added to boiling water, it dissolves and then in a few seconds polymerises, forming a white milky colloidal solution which barely shows signs of settling after a week.

Preparation of Copper Tetrabenzotriazaporphin (V).—An intimate mixture of 5 g. of methylenephthalimidine (2 mols.) (or 7·75 g. of phthalimideneacetic acid), 4·4 g. of phthalonitrile (2 mols.), and 2·5 g. of cupric chloride dried at 100° (1 mol.), spread in a thin layer in a 250 c.c. beaker and immersed in an oil-bath at 250°, soon melted and in a few minutes the separation of a lustrous purple solid began. After 15 minutes' heating, the mass was cooled and ground and the black powder (9 g.) was extracted with hot alcohol until no more brown impurity was removed. The residue (3·9 g.) was purified by continuous extraction with chloronaphthalene. A yellow resinous impurity which sometimes still remained and could be seen by microscopic examination was most conveniently removed by refluxing with a solution of sodium amyloxide (1 g. of sodium in 50 c.c. of amyl alcohol), filtering, and washing. About 2 g. (30% yield) of *copper tetrabenzotriazaporphin* were obtained in needles of "bronzy" lustre very similar in appearance to copper phthalocyanine. When rubbed on paper the crystals gave a greenish-blue smear comparable with that of metal-free phthalocyanine. The substance was insoluble in low-boiling solvents, also in hot or cold pyridine (distinction from Helberger's copper tetrabenzo-mono- and -di-azaporphins) (Found: C, 68·9; H, 3·0; N, 16·9; Cu, 11·5. Found for a sample sublimed in a vacuum at 550°: C, 68·9; H, 2·6. $C_{32}H_{17}N_7Cu$ requires C, 68·9; H, 3·0; N, 17·0; Cu, 11·1%).

Copper tetrabenzotriazaporphin is greener than copper phthalocyanine but otherwise remarkably similar in its properties. It can be obtained in lustrous purple needles by continuous extraction with chloronaphthalene. It is readily soluble to a brown solution in concentrated sulphuric acid, from which it is thrown down as a green flocculent precipitate

on dilution into water. A smear of the compound on paper immediately turns purple when treated with nitrogen peroxide vapour, but regains its original colour in a few hours. The compound sublimes with a greenish-blue vapour at a dull red heat without much decomposition. A characteristic reaction occurs when a few drops of nitric acid are added to a solution of the compound in sulphuric acid : a brilliant red colour is produced, and a blood-red precipitate is obtained when the mixture is poured into water. The red compound is not stable and becomes browner and weaker in shade after a few minutes.

Varying proportions of reactants. In the above preparation, equimolecular proportions of phthalimideneacetic acid and phthalonitrile were taken : under these conditions the formation of copper phthalocyanine or of copper tetrabenzodiazaporphin has never been observed. When 1 mol. of phthalimideneacetic acid was used with 3 mols. of phthalonitrile and 1 mol. of cuprous chloride, an excellent yield (70—80%) of pigment was obtained, contaminated, however, with a small amount of copper phthalocyanine. When 3 mols. of phthalimideneacetic acid were treated with 1 mol. of phthalonitrile and 1 mol. of cuprous chloride, only a yellowish-brown insoluble compound was obtained.

Reaction in the presence of a diluent. A purer product was generally obtained when the reaction mixture was slowly added to 2½ times its weight of chloronaphthalene at 250°. Reaction was very rapid, frothing due to water evolution taking place in the early stages, and the mixture was usually stirred for 30 minutes at 250° before being cooled and worked up in the way already described. The reaction also took place in the presence of pyridine provided that the concentration of the reactants was very high (about 50%).

Sulphonation of Copper Tetrabenzotriazaporphin.—The crude washed reaction product was dissolved in 5% oleum (20 parts) and heated at 100° until a sample diluted with water gave a clear green solution on addition of dilute aqueous ammonia (30—60 mins.). The acid mixture was poured into an excess of cold water and the precipitated sulphonic acid was collected and washed with a little cold water. It could be either dried as the sulphonic acid, or neutralised with ammonia and the solution evaporated to give the ammonium salt. The sulphonic acid was green and only slightly soluble in cold water. The ammonium salt was bluer than the acid and was readily soluble in water to a bluish-green solution.

Preparation of Copper Trichlorotetrabenzotriazaporphin.—A mixture of 13 g. of phthalimideneacetic acid (2 mols.), 9·5 g. of 4-chlorophthalonitrile (2 mols.), and 6 g. of cuprous chloride (1 mol.), added during 10 minutes to 100 c.c. of chloronaphthalene at 250° and mechanically stirred, soon developed a strong green colour and after 30 minutes became viscous. It was heated altogether for 1½ hours at 250° and cooled. The solid product, after being collected and washed with benzene (yield, 12·0 g., dried at 90°), was green and gave the characteristic red colour reaction with a mixture of sulphuric and nitric acids. A pure sample was obtained, as described previously, by washing and extraction, in short thick microscopic needles which gave a bluish-green smear when rubbed on paper [Found : Cl, 15·85; Cu, 9·15 (*i.e.*, 3 atoms of Cl to 1 atom of Cu). *Copper trichlorotetrabenzotriazaporphin*, $C_{33}H_{14}N_7Cl_3Cu$, requires Cl, 15·7; Cu, 9·35%].

Copper Phthalimideneacetate.—To a neutral solution of ammonium phthalimideneacetate prepared from 20 g. of the acid (2 mols.) in 200 c.c. of water, a solution of 11·1 g. of copper sulphate (1 mol.) in 100 c.c. of water was added. The dull greenish precipitate was collected, washed with cold water, and dried (yield, 14·3 g.) [Found : Cu, 14·6. $(C_{10}H_6O_3N)_2Cu$ requires Cu, 14·6%]. *Copper phthalimideneacetate* gave only a trace of pigment when heated with phthalonitrile and copper bronze. When this experiment was repeated quantitatively on a larger scale with and without chloronaphthalene as diluent, only a 10% yield of copper tetrabenzotriazaporphin was obtained (Found : C, 68·85; H, 2·85%).

Methyl Phthalimideneacetate.—The silver salt (10·2 g., prepared from the ammonium salt and silver nitrate in neutral solution) was refluxed for 3 days with 9 c.c. of methyl iodide and 50 c.c. of dry ether. The sticky yellow residue remaining after filtration and evaporation of the solvent was crystallised several times from methanol, giving buff crystals of the *methyl* ester, m. p. 125—127°, in poor yield (Found : C, 64·95; H, 4·3; N, 7·8. $C_{11}H_9O_3N$ requires C, 65·0; H, 4·4; N, 6·9%). The ester gave no trace of pigment when heated with phthalonitrile and cuprous or cupric chloride.

Preparation of Ethylidenephthalimidine (compare Gabriel and Michael, *Ber.*, 1878, **11**, 1013). —(a) 72·5 G. of phthalic anhydride (1 mol.) were dissolved in 130 c.c. (2 mols.) of propionic anhydride at 100°, and 48 g. of sodium propionate (1 mol.) added. The temperature was raised to 160—170° during 15 minutes and maintained for 16 hours; the crystals first formed dissolved after 3 hours. The clear reddish solution was cooled, boiled with 400 c.c. of water,

and, after cooling, the aqueous liquid removed. The heavy brown oil (60 g.) was distilled, and the fraction, b. p. 150—160°/15 mm., collected separately. Yield, 40 g. of a golden-yellow liquid (Found: C, 75·9; H, 5·2. Calc.: C, 75·0; H, 5·0%). 33 G. of the ethylidenephthalide were stirred for 3 days with 50 c.c. of concentrated aqueous ammonia. The reddish-yellow crystalline compound obtained was collected and dissolved in 275 c.c. of alcohol and 75 c.c. of water. The filtered solution deposited 14·6 g. of large yellowish plates, m. p. 209—211°, unchanged by ethylidenephthalimidine prepared by method (b).

(b) A mixture of 130 c.c. of propionic anhydride (2 mols.), 72½ g. of phthalic anhydride (1 mol.), and 56 g. of anhydrous potassium propionate (1 mol.) was heated for 7 hours at 150°, the product boiled with 1 l. of water, and the small oily layer separated. The crystals deposited by the aqueous layer were recrystallised from a mixture of 400 c.c. of glacial acetic acid and 50 c.c. of water, giving 19·3 g. of large crystals of α-phthalidenepropionic acid, m. p. 257—259° (Gabriel and Michael, *loc. cit.*, give m. p. 245—248°) (Found: C, 64·6; H, 3·6. Calc. for $C_{11}H_8O_4$: C, 64·7; H, 3·9%). 8·4 G. of the acid were dissolved in 8 c.c. of concentrated aqueous ammonia and 80 c.c. of water and after 30 minutes the solution obtained was acidified with hydrochloric acid until it was acid to Congo-paper and kept in ice overnight; the white precipitate produced was washed with cold water and dried at 40° (yield, 6·1 g.). 1·1 G., crystallised from 20 c.c. of alcohol, gave 0·5 g. of large clear colourless plates of ethylidenephthalimidine, m. p. 210—212° (Found: C, 76·1; H, 5·7; N, 9·0. Calc. for $C_{10}H_9ON$: C, 75·4; H, 5·7; N, 8·8%). Gabriel and Michael (*loc. cit.*) reported the formation of phthalidenepropionamide, m. p. 193—195°, from ammonia and α-phthalidenepropionic acid by a process similar to that described above.

Preparation of Benzylidenephthalimidine.—A vigorous stream of ammonia was passed for 5 hours into 129 g. of molten benzylidenephthalide at 200°. The product separated from glacial acetic acid in heavy yellow crystals (70 g.), m. p. 184—185° (dried at 40°) (Found: C, 81·3; H, 4·5; N, 6·5. Calc. for $C_{15}H_{11}ON$: C, 81·4; H, 5·0; N, 6·4%). A further 35 g. of less pure product were obtained by concentration of the filtrate. Gabriel (*Ber.*, 1885, **18**, 2433) gives m. p. 182—183°.

The author thanks Imperial Chemical Industries, Ltd., and the Directors of the Dyestuffs Group for permission to publish this investigation.

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